Real-Time Small Angle X-ray Scattering Study of Two-Stage Melt Crystallization of Peek

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Abstract No. Geor6394
Beamline(s): **X12B**

Introduction: One of the many important problems in polymer physics that can be studied by X-ray scattering is structure formation, and its relationship to observations of multiple endothermic peaks seen in high performance polymers. Assignment of scattering peaks to structural entities within the material, the relative perfection of the crystals, and the possibility of their reorganization, are all influenced by the melt processing history. With the advent of high intensity synchrotron sources of X-radiation, polymer scientists gain a research tool which, when used along with thermal analysis, provides structural information about the crystals during growth and subsequent melting.

Methods and Materials: The subject of our present study is Poly(etheretherketone), PEEK. It has a very high glass transition temperature (145°C) and crystal melting point (337°C-342°C) making it suitable for high performance engineering applications in aerospace, automotive and electronics industries. In nearly all-thermal studies, isothermally crystallized PEEK shows dual endotherms. Small angle X-ray scattering (SAXS) and thermal studies have been used to address the formation of this dual endothermic response which has been variously ascribed to insertion of later-forming lamellar crystals between previously formed lamellae, existence of distinct dual crystal populations, or melting of crystals followed by immediate re-crystallization.

Results: As the holding time at 280°C increases, a weak shoulder grows up on the high-s side of the Bragg peak. An arrow marks the shoulder in **Figure 1**. After 10 min. at 280°C the intensity in the shoulder is as large as intensity in the main Bragg peak. When the temperature first increases from 280°C to 295°C, the weak shoulder diminishes, and then increases once again as the holding time at 295°C increases. When the non-isothermal heating begins, and the temperature reaches 305°C, the intensity on the high s side decreases. As temperature increases, the Bragg maximum shifts to lower s.

Conclusions: During two-stage melt crystallization, dual populations of crystals form during the first stage regardless whether the treatment conditions are a low-to-high or high-to-low temperature sequence. During the first stage, the average long period and crystal thickness decrease, while linear stack crystallinity increases, with an increase in holding time. In the low-to-high temperature sequence, heating to the second stage melts a population of least perfect crystals. A small intensity shoulder at high s decreases upon heating through the lower of the two endotherms, while the average long period, crystal thickness, and linear stack crystallinity all increase. During the holding at the second stage, additional crystals form. Scattered intensity increases in the high s shoulder, and average long period and crystal thickness decrease as some of the now-molten material recrystallizes.

Acknowledgments: The National Aeronautics and Space Administration, Grant NAG8-1167 supported this work.

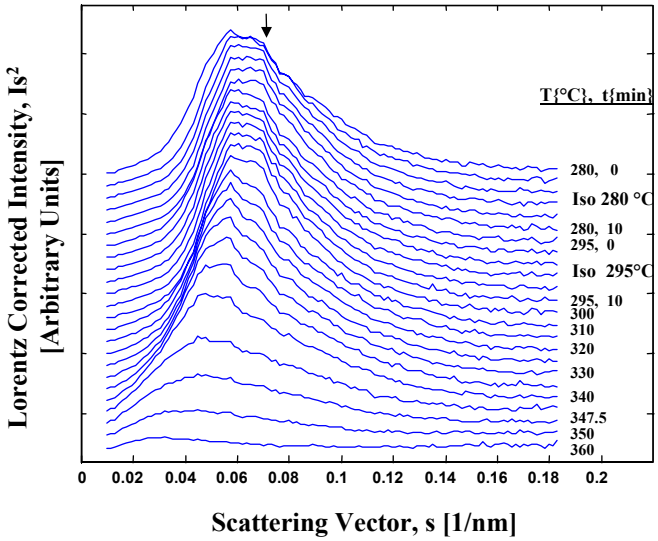

Figure 1. Lorentz corrected intensity vs. scattering vector for PEEK at a sequence of temperatures and times during “low-to-high” crystallization and melting.